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Removal of Hexavalent Chromium Using Activated Carbon Prepared from Teak Wood Waste Biomass

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ABSTRACT

The present work reported the adsorption of Cr (VI) from aqueous solutions on activated carbon prepared from teak wood waste. Biomass from teak wood were taken out and pulverized in a micro-pulverizing mill. The powder thus obtained was activated with 40% H_3PO_4 and carbonized at 600 °C for 1 hour in an inert atmosphere. Physico-chemical characteristics such as functional groups and surface morphology of the activated carbon were analyzed using FTIR spectroscopy and SEM analysis respectively. Batch adsorption experiments were performed to investigate the effects of Cr (VI) concentration, carbon dose, pH and time. The maximum adsorption capacity of Cr(VI) was found to be 1.5 g/L at pH 3 and temperature 30±1 °C. The Freundlich adsorption isotherm best represented the equilibrium data and a pseudo-second order relation represented the adsorption kinetics.

Keywords: Activated carbon, Cr(VI) removal, SEM, kinetics, adsorption isotherms

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INTRODUCTION

The release of heavy metals into wastewater through human and industrial activities has become a major problem both to humans and aquatic lives[1]. Chromium as a heavy metal is ranked among the top sixteen toxic pollutants that have harmful effects on human health[2]. High chromium dosage has been reported to cause damage to human kidney and the liver[3]; and at low concentration it causes skin irritation and ulceration[4]. Exposure to high chromium concentration also causes cancer in the digestive tract and lungs[5]. Therefore, indiscriminate discharge of heavy metals in general into aquatic bodies and sources of potable water has to be regulated through enactment of legal standards and strict environmental control mechanism[6]. For the removal of dissolved heavy metal ions, several techniques such as solvent extraction, ion exchange, membrane process, electro dialysis, precipitation, phyto extraction, ultra filtration, reverse osmosis and adsorption have been tested. These methods except adsorption are non-economical with disadvantages such as incomplete metal removal, high reagent cost, energy requirements and generation of toxic sludge or other waste products that require further disposal or treatment. The adsorption technique remains the most preferred method because of its efficiency and low cost[7].

Many investigations have been carried out on the effective removal of heavy metals from solution using natural adsorbents derived from agricultural wastes[8]. The present study is therefore carried out to investigate the possible use of teak wood waste material, for the removal of chromium ions from aqueous solution. The effects of some parameters such as, contact time, solution pH, adsorbent dose and initial chromium ions concentrations on the performance of the adsorbent on the sorption process were investigated. Scanning electron microscopy (SEM) and Fourier transform infrared spectroscopy (FTIR) were used to analyze the possible mechanism of the adsorption process. The equilibrium data were analyzed using Langmuir and Freundlich isotherm models.

MATERIALS AND METHODS

Adsorbents: The teak wood waste biomass material was collected and air dried for 15-20 days. The dried material was cut into small pieces for further chemical modification. The ground material was mixed with equal amount of concentrated phosphoric acid and stirred for 30 min. The acid- plant material slurry was placed in a beaker and dried at 80 °C in a hot air-oven. After 24h, the thermo chemical reaction between acid and plant materials, it was proceeding by raising the oven temperature to 120 °C for 90 min. After cooling, the resulting carbon washed with distilled water until a constant pH of the slurry reached. The wet carbon material was dried at 110 °C and sieved into discrete particle size and stored. The adsorbent after phosphoric acid treatment was designated as TPAC. All the chemicals used throughout the study were supplied by so fine chemicals,

E.Merck, India. All the adsorption experiments were carried out at room temperature (30 ± 1°C).

Adsorbate: A stock solution of Cr (VI) was prepared (1000 mg/L) by dissolving required amount of Potassium dichromate salt, $K_2Cr_2O_7$ in distilled water. The stock solution was further diluted to obtain desired concentration ranging from 20 to 100 mg/L.

Batch experiments: Batch equilibrium experiments were conducted by adding 100 mg biomass to Erlenmeyer flask containing 50 ml of different test solutions at desired pH conditions. The initial solution pH was adjusted by using 0.1 M HCl or 0.1 M NaOH. The flasks were agitated at 150 rpm in a rotary shaker. After 3 hrs of contact time, the biomass was separated from the test solution by filtration. The chromium ion content in the supernatant liquid was determined using photoelectric calorimeter. Prior to analysis, the equipment was initially calibrated using standard chromium ion solution. The amount of chromium ion adsorbed by biomass was calculated from the difference between the concentration of chromium ion in test solution and the concentration of chromium ion in the supernatant liquid. The amount of adsorption at equilibrium (q_e mg/g) and sorption efficiency (%) were calculated according to the expressions:

q_e (mg/g) = (C_o – C_e) V / m ---------(1)

Sorption efficiency % =[(C_o – C_e) / C_o] X 100 ----------(2)

Where C_o and C_e are the initial and equilibrium concentrations (mg/L), V the volume of solution (L), m is the mass of the activated carbon (g).

RESULTS AND DISCUSSION

FTIR analysis of activated carbon

The surface chemical characteristics of TPAC were determined by Fourier Transform Infrared Spectroscopy (FTIR), and the spectrum is given in Fig. 1. The peak at 3407 cm^{-1} is attributed to the stretching vibration of O–H band and aliphatic, asymmetric C–H stretching vibration of methylene group[9]. The peaks at 2924 cm^{-1} in the spectra are due to stretching vibration of C-H. The band at 1750–1700 cm−1 represents the acidic carbonyl C=O stretching. The peak at 1707 cm−1 is attributed to the vibration of –COOH band[10,11]. The peaks around 1000–1300 cm−1 presents C-O stretching in phenols, alcohols, acids, ethers and esters. These groups participate in Cr(VI) adsorption to TPAC. The surface of carbon materials is, in general, rich in a variety of surface functional groups among which the C–O type groups are predominant and they form in ethers, acids and esters. FTIR analysis confirmed the presence of carboxylic and phenolic surface groups on the TPAC. There are hydroxyl groups (3407 cm^{-1}; O–H stretching mode) present in the IR spectrum of the functionalized TPAC (see Fig. 1).

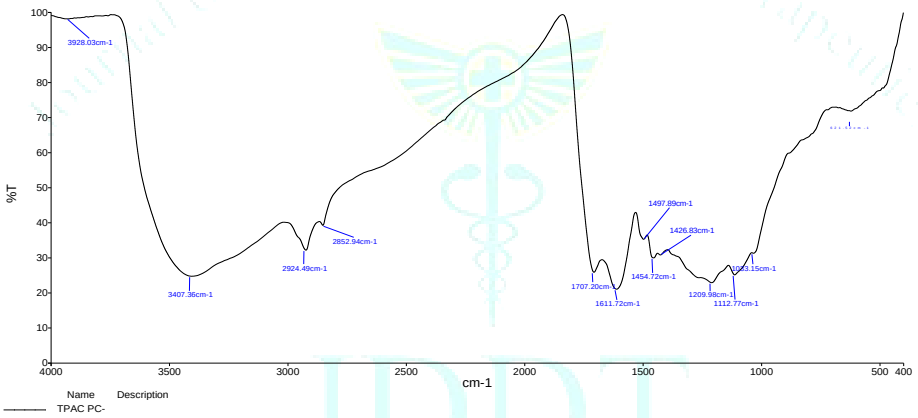

Fig.1: IR spectrum of activated carbon TPAC

The SEM micrograph of TPAC before adsorption is shown in Fig. 2. It is seen that TPAC has a highly porous structure.

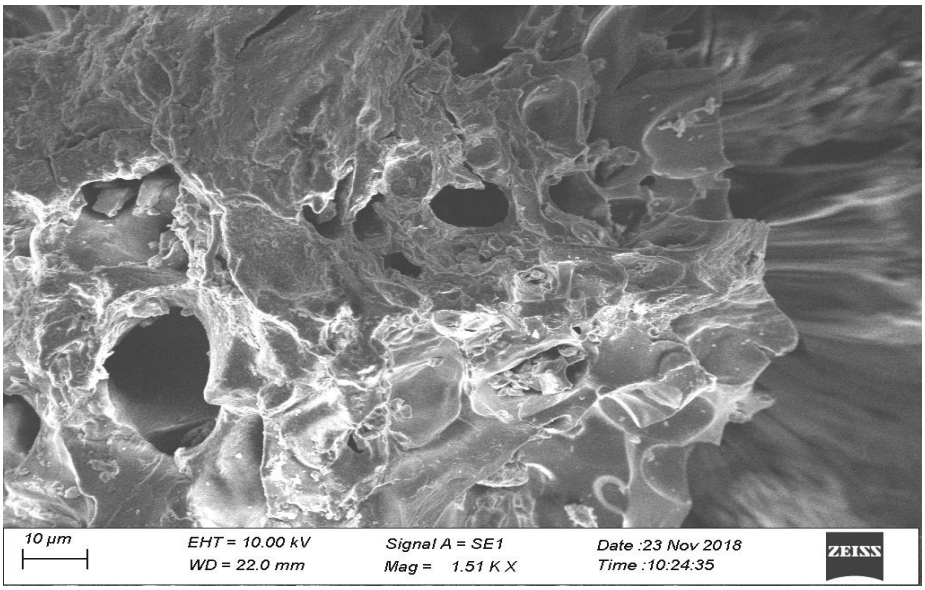

Fig.2: SEM image of TPAC

Effect of pH

About 50 ml of 50 ppm chromium aqueous solutions were prepared and the pH were adjusted by using 0.1 M HCl /0.1 M NaOH. Each solution was treated with 100 mg of the adsorbent and kept for a contact time of 3 hours at room temperature with intermittent shaking. The residual chromium ion concentrations were measured. Maximum adsorption occurred at 92.0 % at pH 3 (Fig.3) and the reasons were as follows: Analysis from the perspective of adsorbate: in aqueous solution, Cr (VI) mainly exists in three forms[12] of CrO_4^{2-}, $Cr_2O_7^{2-}$ and $HCrO_4^-$. With the change of solution pH, the form of will change accordingly. When the solution is acidic, Cr (VI) is mainly distributed in the form of $HCrO_4^-$, the study found that $HCrO_4^-$ can form stable compounds with adsorbent. In the acidic conditions, the oxidation of Cr (VI) is very strong, the oxidation and reduction on the removal of Cr (VI) to make a contribution. Therefore, the removal rate is high under acidic conditions. When the pH of the solution increases gradually, the Cr (VI) in the solution begins to be dominated by CrO_4^{2-} and $Cr_2O_7^{2-}$; With the concentration of OH^- increases, and the competitive adsorption of with Cr (VI) results in inhibition of the adsorption of Cr (VI). So under acidic conditions, the removal rate of Cr (VI) is higher than that under alkaline condition.

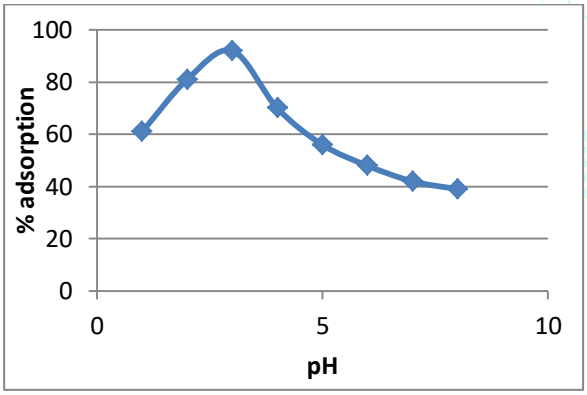

Fig.3: Effect of pH on removal of Chormium using TPAC; Initial con-50mg/l; Time : 3 hrs; Wt. of adsorbent – 100 mg; Temp = 30°C ±1

Effect of Activated Carbon Dosage on Adsorption of Cr (VI)

The dosages of activated carbon respectively are 0.2g, 0.6g, 1.0g, 1.5g, 2.0g and 2.5g; The concentration of Cr (VI) solution is 10 mg/L; the temperature is at room temperature; the adsorption time is 120min; the solution pH is 3. The effect of activated carbon dosage on removal of Cr (VI) is shown in Fig.4. In the picture, it can be seen that when the activated carbon dosage increased from 0.2g to 2.5g, the removal rate of Cr (VI) increased from 15.86% to 96.46%, showed a rising trend. Analysts believe that with the increase of the amount of activated carbon, the available adsorption sites in the contact reaction increased correspondingly. The amount of Cr (VI) adsorbed by activated carbon increased, which showed that the removal rate increased with the increase of dosage . It is also found that the amount of adsorption decreases with the increase of dosage. The reason is that the dosage increases and the specific surface area increases, so more Cr (VI) is adsorbed on the surface of activated carbon, but the unit surface utilization of adsorbent decreases. Thus, the amount of activated carbon is not the more the better. From the above analysis, 1.5 g/L was selected as the best dosage for removing of Cr (VI).

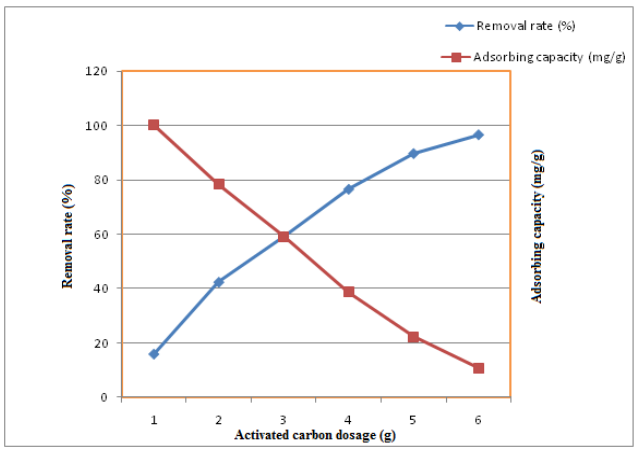

Fig.4: The effect of activated carbon dosage on removal of Cr (VI)

Initial Concentration

To 50 ml solutions of each 10 to 50 ppm of chormium ion solution, 100 mg of TPAC powder was added and left for a period of 3 hours at room temperature (30±1°C) with intermittent shaking. Appropriate control flasks without adsorbent were also maintained. The results of adsorption were recorded to calibrate the equilibrium time. The effect of initial concentration on the removal of chromium ion shown in Fig.5.

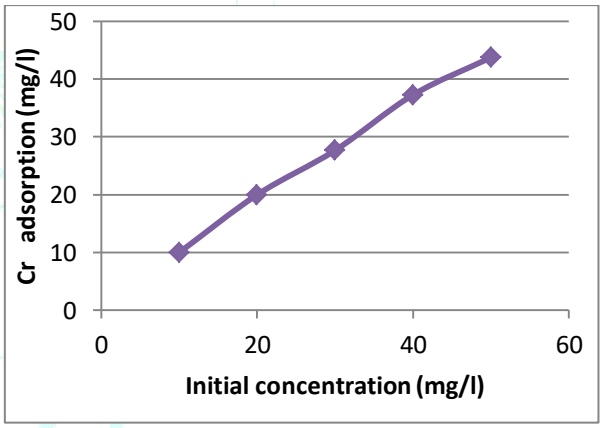

Fig. 5: Effect of Initial concentration on removal of chromium using TPAC (pH = 3)

Effect of Contact Time

As shown in Fig.6 , the extent adsorption increases steeply with increasing contact time and tends to a constant value. In the beginning all the active sites on the adsorbent are vacant hence adsorption proceeds at a faster rate and desorption at a lower rate, the net effect is faster increase in the extent of adsorption. As the active sites get occupied, the rates of adsorption and desorption tend to be equal and extent of adsorption reduces and eventually becomes nearly constant at equilibrium. Any further adsorption beyond this is through intra-particle diffusion which is a much slower process[13,14]. For the given situation adsorption equilibrium time is observed to be 150 min.

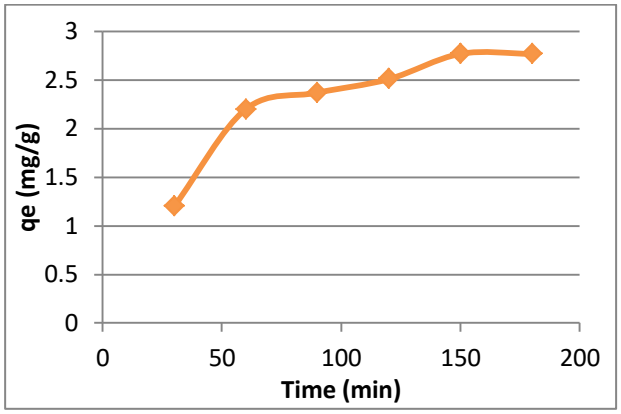

Fig.6: Effect of contact time on removal of chromium using TPAC (pH = 3; Wt. of adsorbent = 100mg; Initial concentration : 30 mg/l; Temp = 30±1 °C)

Adsorption isotherm studies

For solid–liquid adsorption system, the adsorption behavior can well be described by adsorption isotherm model[15] [15]. The adsorption isotherm can indicate the distribution of adsorbate molecules between the solid phase and the liquid phase at equilibrium. Equilibrium is said to be established when the concentration of adsorbate in bulk solution is in dynamic balance with that on the liquid adsorbate interface. It is significant to understand the adsorption behavior in order to describe adsorption process using appropriate adsorption isotherm model. Therefore, the distribution of Cr(VI) ions between the adsorbent and solution was determined by Langmuir and Freundlich adsorption isotherms by fitting the equilibrium adsorption data into their respective isotherm equations[16,17].

Freundlich adsorption isotherm

The Freundlich equilibrium isotherm model describes adsorption by heterogeneous energetic distribution of adsorption sites accompanied by interaction between solute molecules (Eq. 3).

Freundlich equation:

$$\left(\frac{x}{m}\right) = k\,C_e^{1/n} \qquad \text{----------(3)}$$

where n is the Freundlich constant and k is adsorption coefficient, x/m is the amount of Cr(VI) ions adsorbed per unit amount of adsorbent and C e is Cr(VI) concentration at equilibrium in aqueous phase. Logarithmic form of eqn (3) as follows:

$$\log\left(\frac{x}{m}\right) = \log k + \frac{1}{n}\log C_e \qquad \text{----------(4)}$$

$$\log q_e = \log k + \frac{1}{n}\log C_e \qquad \text{----------(5)}$$

Where $x/m=q_e$. The Freundlich isotherm and the Langmuir isotherm apply to TPAC adsorbate system. The isotherm giving an R^2 value closest to unity was deemed to provide the best fit. The Freundlich model has contained two useful parameters (k and n)[18,19].

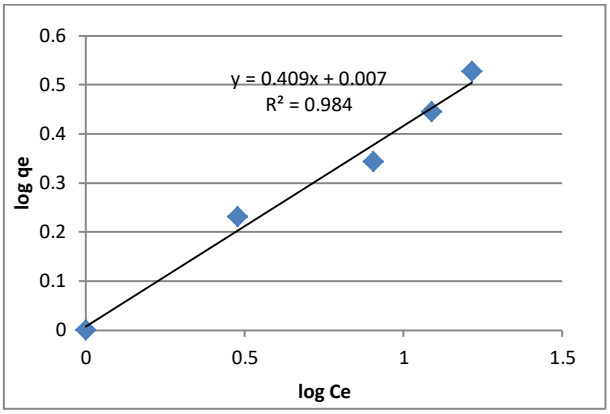

Fig.7: Freundlich plot

Langmuir adsorption isotherm

The equilibrium adsorption data for the concentrations of Cr(VI) ions was fitted into the linear form of Langmuir's isotherm equation(6) to determined the distribution of Cr(VI) ions between the adsorbent and solution:

$$\frac{C_e}{q_e} = \frac{1}{q_0 b} + \frac{C_e}{q_e} \qquad \text{---------- (6)}$$

Where Ce is the equilibrium concentration of the chromium ions in solution (mg/L), q_e is the equilibrium concentration of Cr(VI) ions on the TPAC adsorbent (mg/g), q_0 and b are Langmuir constants related to sorption capacity and the rate of adsorption respectively.

Maximum adsorption capacity (q_0) is the monolayer capacity of the adsorbent (mg/g) and b is the Langmuir adsorption constant. A plot of Ce/qe against Ce over the entire concentration range is a straight line with a slope of $1/q_0$ and the intercept of $1/ q_0b$.The correlation coefficient (R^2) value is 0.978.

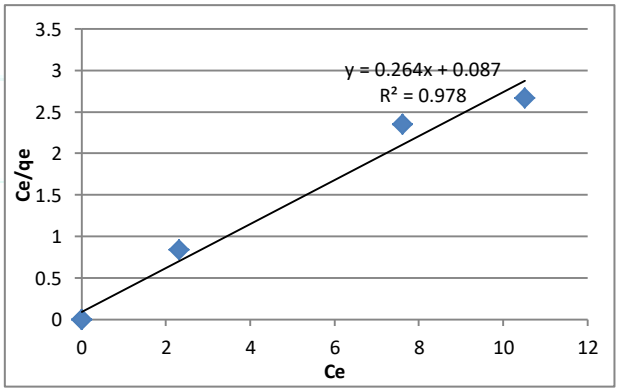

Fig. 8: Langmuir isotherm (pH = 3 ; Particle size : 0-63 µ; Wt. of adsorbent = 100mg; Time : 150 minutes ; Temp = 30±1°C)

Among the Freundlich and langmuir model studied, the correlation coefficient (R^2) value is 0.984 which is very close to 1 indicating that the adsorption follows the Freundlich isotherm

Kinetic study

The kinetics of Cr (VI) sorption on the TPAC activated carbon as adsorbent was analyzed using two kinetic models. The linearized form of pseudo-first-order kinetic model[20] and the pseudo-second-order sorption kinetics can be expressed as shown in Fig.9 and Fig.10. and show the plots of experimental data at different initial concentration of Cr(VI) for pseudo-first order and second order, models,

respectively. The calculated kinetic parameters are presented in Table. Closure agreement between experimental and calculated kinetic constants and coefficient of correlation closure to unity indicated that the pseudo second order model better represents the experimental data.

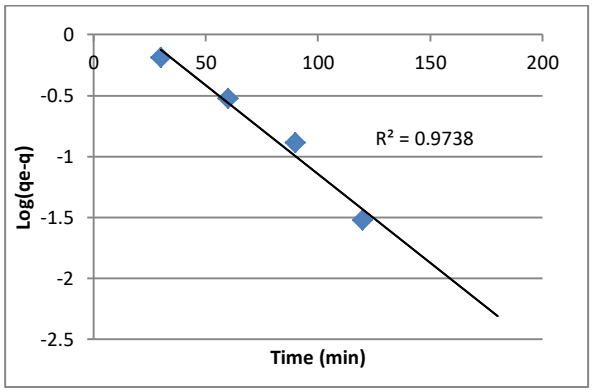

Fig. 9: Pseudo first-order plot for the adsorption of Cr (VI) by activated TPAC for adsorbent dosage 20 mg /lit and concentration 100 mg/lit

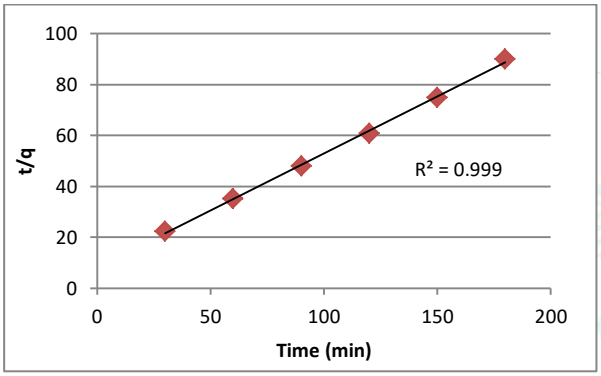

Fig.10: Pseudo-second-order kinetic model for removal of Cr (VI) by TPAC (Solution pH: 3; Wt. of adsorbent = 100mg; Initial concentration : 10 mg/l Temp = 30±1°C).

CONCLUSION

The results indicate that the teak wood biomass activated carbon is a good sorbent. The adsorption of Cr(VI) was found to be highly dependent on the pH value of the system, with the best results being obtained at pH 3. A high percentage of Cr(VI) may be reduced to the Cr(III) form at low pH values. The FTIR spectra showed that the hydroxyl group was the chromium binding site within the pH range (pH 1-4) where chromium does not precipitate. Chromium (VI) was rapidly adsorbed when lower concentrations were used. The isotherm data were analyzed by the Langmuir and Freundlich isotherms and the data fitted Freundlich model better than the Langmuir isotherm model. The kinetic data were well fitted by a pseudo-second order model.

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